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### (54) BUILDING PRODUCTS

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**Description****TECHNICAL FIELD**

5 [0001] This invention relates to low density building products and methods for their production.

**BACKGROUND ART**

10 [0002] Shaped calcium silicate products are widely used in industry and domestic applications as thermal insulation and refractory materials and shown in Australian Patent No 552,930. These products are commonly formed by combining a source of calcium hydroxide with a siliceous material at elevated temperature and pressure. A variety of crystalline forms of calcium silicate may be formed depending upon the temperature, pressure, length of reaction time and water concentration used. The resultant slurry of hydrated calcium silicate crystals may then be cast into moulds and dried, usually by the application of heat, to form the desired finish shaped products prior to moulding if desired.

15 Reinforcing fibres such as glass and polyester fibres may then be added to the slurry.

20 [0003] Such pure calcium silicate products, however, do not have sufficient strength, toughness and durability for various building applications. Various mechanisms have been proposed for producing calcium silicate products with sufficient strength for building applications. Low density calcium silicate boards using fibre contents of 3% by weight or less are well known in fire protection applications. The method of manufacture of the calcium silicate in these products and the other ingredients needed for high temperature (> 1000°C) stability make such products uneconomical for use as commodity products. For example, US Patent No 5,547,505 discloses a production method for low heat cements with good compressive strength and heats of hydration. The process is, however, quite complex. It involves the mixing of calcareous materials, siliceous materials and aluminous materials, melting the mixture, quenching the melt and grinding the quenched matter for inclusion in the cement composition.

25 [0004] Australian Patent No 606,344 attempts to overcome the difficulties associated with calcium silicate products by adding fibrous materials, such as wood pulp, and a suitable polymeric coagulant, forming thin sheets of the resulting material and laminating the sheets to form a building board. Various other production techniques or additives such as fibres, polymeric binders etc have been used to increase the strength and durability of the calcium silicate product. German Patent Application DE 3711549 for example includes a polymeric binder and an expansion ettringite forming agent to the calcium silicate slurry to give a product similar to wood.

30 [0005] Fibre reinforced cement products such as water resistant building sheets have been used for building since 1895. In recent history reinforcing fibres used in such products have included not only asbestos fibres, but also cellulose fibres (AU 515151), metal fibres, glass fibres and other natural fibres. Typically the density of such building sheets is from 1.2-1.7 g/cm<sup>3</sup>, the variation in density typically being achievable by compression and dewatering of the fibre cement slurries used in manufacture and by varying the amount of fibre used.

35 [0006] The densities of the building sheets described above mean the products are heavier than timber based products of equal dimension and consequently are more difficult to cut, machine and nail than timber and timber based products. In this regard, the density of natural timber sheets typically range from 0.7 to 0.9g/cm<sup>3</sup> for dry hardwoods and from 0.38 to 0.6 g/cm<sup>3</sup> for dry softwoods. The dry density of reconstituted pressed hardboards typically range from 40 0.95 to 1.1 g/cm<sup>3</sup>.

40 [0007] It would be desirable to manufacture building sheets having a density similar to that of timber thus enabling lighter, more nailable, easier to cut and easier to machine products whilst retaining the durability, fire resistance, rot proofness and water resistant properties of the fibre reinforced cement product.

45 [0008] It is an object of the present invention to substantially ameliorate at least some of the above-mentioned disadvantages of the prior art or at least provide a commercial alternative thereto.

**DISCLOSURE OF THE INVENTION**

50 [0009] According to a first aspect, the present invention provides a method for forming a cementitious product comprising adding a cementitious material, a siliceous material and a low bulk density material to water to form a slurry forming a green shaped article from the slurry and curing the article in an autoclave, characterised in that the low bulk density material is a mixture of calcium silicate hydrate and unreacted siliceous reactant

55 [0010] The applicant proposes to use calcium silicate hydrate as a density modifier since unlike commonly used materials such as vermiculite, perlite or EPS foam beads, it does not float and it resists crushing.

[0011] The low bulk density material is made up of particles being substantially calcium silicate hydrate, typically in the form of a 3-D interlocking structure containing beads and is resistant to crushing in subsequent processing.

[0012] Preferably the low bulk density material has a bulk density between 0.06 and 0.3 g/cm<sup>3</sup>.

[0013] In another preferred embodiment, the low bulk density material is provided by reacting a siliceous reactant

with a calcareous reactant in the presence of water under pressure and elevated temperature, wherein at least 90 wt % of the siliceous material has a particle size of less than 100 microns (100  $\mu\text{m}$ ).

[0014] According to the inventive process for forming a cementitious product, the green shaped articles may be formed from the water borne slurry by any of a number of conventional processes such as the Hatschek sheet process, the Mazza pipe process, the Magnani sheet process, injection moulding, extrusion, hand lay-up, moulding, casting, filter pressing, flow on machine, roll forming, etc., with or without post-formation pressing. After forming, the green article is preferably pre-cured for a short time preferably up to 80 hours, then cured by autoclaving preferably in a steam pressurised vessel at 120 to 200°C for 3 to 30 hours, most preferably for less than 24 hours. The length of time and temperature chosen for curing is dependent on the formulation, the manufacturing process and form of the article.

[0015] The applicant has also found that it is possible to provide a low bulk density material which is substantially composed of calcium silicate hydrate for use in a building product without it being necessary to ensure full conversion of the reactants to calcium silicate hydrate. In a preferred embodiment this reaction is terminated prior to complete conversion of the reactants to calcium silicate hydrate. Preferably the reaction is terminated at less than 4 hours. More preferably the reaction is conducted over a period of up 2 hours such that at least 80% of the calcareous reactant material is converted into calcium silicate hydrate (preferably as determined from DTA (differential thermal analysis)/TGA (thermogravimetric analysis)).

[0016] The applicant has found that the product resulting from the reaction between the siliceous reactant material and the calcareous reactant material at elevated temperature and pressure even at very short reaction times, eg down to ½ hour with appropriate apparatus, is suitable for use in building products such as fibre reinforced sheets. Such short reaction times clearly provide advantages both in terms of cost and speed of production.

[0017] The product resulting from this reaction not only serves as an effective density modifier for producing cementitious products resulting in densities of 1.2 g/cm<sup>3</sup> to 0.5 g/cm<sup>3</sup> and if combined with aeration of the slurry, the density may be even lower, but provides other advantages including high strength and low surface water permeability.

[0018] Another advantage of producing such low density cementitious products in accordance with the invention is that thicker sheets or thicker walled products can be manufactured, including those containing fibres, without being excessively heavy for handling. In addition such thick sheets, for example 10 mm-35 mm thick, are able to be nailed or machined (which is not always possible with normal density or compressed fibre cement sheets). The low density cementitious products of the invention are also suitable for fixing with power driven nail guns since the lower density of the board enables the impact and head of the nail to be absorbed into the board unlike normal density or compressed fibre cement boards which may fracture by the impact of the head of the nail. The low density of the inventive cementitious products also enables for example sheets of say up to 12 mm thickness x 1200 mm wide to be scored and snapped. Normal density fibre cement sheets would be too strong and dense to score and snap at such dimensions.

[0019] Even at densities below 0.5g/cm<sup>3</sup> the cementitious products resulting from the present invention have surprisingly good strength and toughness. The applicants have also noticed that the low density cementitious products resulting from the inventive process have lower water surface permeability as compared with conventional cementitious products.

[0020] The siliceous reactant material may be obtained in the correct particle size or alternatively ground by any appropriate method including a high impact type ball or rod mills, vertical stirred ball mill or attritor mill. Such mills obtain high particle size reduction rates by impact fracture of particles. The siliceous reactant material preferably has particle size of 90 wt % less than about 100 micron (100  $\mu\text{m}$ ) more preferably less than 70 micron and most preferably less than 50 micron (50  $\mu\text{m}$ ) diameter (as measured on a laser diffraction particle size analyser such as a Malvern Mastersizer diffraction type particle size analyser).

[0021] Suitable siliceous reactant materials are crystalline, most preferably such as quartz, quartzite sand, quartzite rock or crystalline silica. Amorphous siliceous reactant materials can also be used but are less desirable. Typical amorphous siliceous materials include diatomaceous earth, silica fume, rice hull ash, fly ash, blast furnace slag, granulated slag, steel slag, crystalline or air cooled slag, geothermal silica and mixtures thereof. The siliceous material in steps (a) and (c) may be the same or different.

[0022] The silica particle size may be adjusted if desired to alter reaction rates for forming the substantially calcium silicate hydrate product. Other process parameters or additives may be altered to adjust the various properties of the resultant building product including density, toughness etc.

[0023] Suitable calcareous materials include lime particularly quick lime preferably containing greater than 90% CaO. Quick lime can be hydrated by slaking it in water, preferably at a temperature of 40° to 70°C in a ratio of 1 to 7 litres of water per kilogram of lime.

[0024] Water in the reaction is typically present in an amount to up to 30 times the total weight of the siliceous and calcareous reactant materials.

[0025] Suitably the siliceous material and calcareous material are reacted at a temperature between 120°C and 250°C, more preferably at a temperature of between 160°C and 180°C.

[0026] Preferably the siliceous and calcareous materials are reacted in a stirred pressure vessel. Suitable pressures

used are typically between 200 and 4000 kPa, more preferably between 600 and 1000 kPa.

[0027] Typically, the calcareous material and siliceous material are reacted in a molar ratio of CaO:SiO<sub>2</sub> of from 0.1 up to 1.2. More preferably they are reacted in a ratio of 0.3-0.8.

[0028] The present invention further provides a formulation for preparing a cementitious product comprising:

5

a cementitious material  
a siliceous material, and  
a low bulk density material being a mixture of calcium silicate hydrate and unreacted siliceous reactant.

10 [0029] Throughout this specification, unless indicated otherwise where there is reference to wt %, all values are with respect to the formulation on a dry ingredients weight basis prior to addition of water and processing.

[0030] The siliceous material is preferably present in the dry formulation in an amount of from 10 to 80 wt %, more preferably 30 to 70 wt %, most preferably 40 to 65 wt %. Preferably the siliceous material is ground sand (also known as silica) or fine quartz and has an average particle size of 1 to 500 microns, more preferably 20 to 70 microns.

15 [0031] The cementitious material is preferably present in the dry formulation in an amount of from 10 to 80 wt %, more preferably 20 to 70 wt %, most preferably 30 to 40 wt %. Suitable cementitious material is cement and/or lime and/or lime containing material and includes Portland cement, hydrated lime, lime or mixtures thereof. Preferably the cementitious material has a fineness index of 200 to 450m<sup>2</sup>/kg and more preferably 300 to 400m<sup>2</sup>/kg.

20 [0032] It will be appreciated that the siliceous material and cementitious material may originate from separate source materials eg silica and Portland cement or can originate from a single source material eg a blended cement which is a cement including ordinary Portland cement and/or off-white cement with one or a combination of limestone, granulated slag and condensed silica fume. The proportion of these additions is in excess of 5% by mass.

[0033] Similarly, the siliceous reactant material and calcareous reactant material can be provided from separate sources eg silica and limestone or from a single source material eg a siliceous limestone deposit.

25 [0034] The low bulk density calcium silicate hydrate of the invention is preferably added in an amount of up to 80 wt %, more preferably up to 50% of the dry formulation.

[0035] The cementitious product can include a fibrous material capable of producing a fibre reinforced product. Suitable fibrous materials can include asbestos however it is more preferable to use non-asbestos fibres including cellulose such as softwood and hardwood cellulose fibres, non wood cellulose fibres, mineral wool, steel fibres, synthetic polymer fibres such as polyamides, polyesters, polypropylene, polymethylpentene, polyacrylonitrile, polyacrylamide, viscose, nylon, PVC, PVA, rayon, and glass, ceramic or carbon. When cellulose fibres are used, they are preferably refined to a degree of freeness of between 20 and 800 Canadian Standard Freeness (CSF), more preferably 200 to 500 CSF. Thermomechanically or chemically refined fibres are preferred. Cellulose fibres produced by the Kraft process are suitable. The cellulose fibres may be bleached, unbleached, partially bleached or mixtures thereof. The fibrous materials may be present in a concentration of 0 to 25 wt %, preferably 2 to 16 wt %, more preferably 5 to 14 wt % based on the weight of the dry formulation.

35 [0036] The density of the cementitious product material resulting from the present inventive process will depend upon a number of factors including the quantity of low density substantially calcium silicate hydrate material and fibrous material or pulp added to the mix. Shown below in Tables 1, 2 and 3 are saturated, equilibrium and oven-dried densities of cementitious product resulting from the present inventive process with varying amounts of CSH material and pulp.

#### DENSITY (g/cm<sup>3</sup>) MODIFICATION OF FIBRE REINFORCED CEMENTITIOUS PRODUCT WITH CSH MATERIAL AND PULP

45 [0037]

TABLE 1 -

WATER SATURATED				
CSH %	DENSITY WITH 8.25% PULP			DENSITY WITH 14.25% PULP
0	1.700	1.650		1.590
10	1.600	1.570		1.530
20	1.520	1.500		1.470
30	1.440	1.440		1.420

TABLE 1 - (continued)

WATER SATURATED				
5	CSH %	DENSITY WITH 8.25% PULP	DENSITY WITH 11.25% PULP	DENSITY WITH 14.25% PULP
10	40	1.420	1.380	1.360
15	50	1.340	1.320	1.320

TABLE 2 -

ATMOSPHERIC EQUILIBRIUM (nominally 25°C and 50% relative humidity)				
15	CSH %	DENSITY WITH 8.25% PULP	DENSITY WITH 11.25% PULP	DENSITY WITH 14.25% PULP
20	0	1.334	1.188	1.178
25	10	1.132	1.035	1.021
	20	1.036	0.815	0.897
	30	0.969	0.779	0.800
	40	0.920	0.682	0.748
	50	0.641	0.596	0.608

TABLE 3 -

OVEN DRIED (100°C 24 hours)				
30	CSH %	DENSITY WITH 8.25% PULP	DENSITY WITH 11.25% PULP	DENSITY WITH 14.25% PULP
35	0	1.127	1.161	1.115
40	10	1.045	1.011	0.966
	20	0.912	0.880	0.864
	30	0.794	0.771	0.767
	40	0.702	0.684	0.669
	50	0.617	0.587	0.591

45 [0038] The cementitious product may also contain 0 to 40 wt % of other additives such as fillers, for example, mineral oxides, hydroxides and clays, metal oxides and hydroxides, fire retardants, for example, magnesite or dolomite, thickeners, silica fume or amorphous silica, colorants, pigments, water sealing agents, water reducing agents, setting rate modifiers, hardeners, filtering aids, plasticisers, dispersants, foaming agents or flocculating agents, water-proofing agents, density modifiers or other processing aids. Specific additives can include aluminium powder, kaolin, mica, metakaolin, silica fume and calcium carbonate.

50 [0039] In a preferred embodiment, the low density cementitious products are formed by the Hatschek process. For use with the inventive low density cementitious composition, however, certain modifications to the Hatschek process may be required or desired.

55 [0040] Firstly, with the low density cementitious composition, delamination of the green sheet may occur when the vacuum pad contacts the sheet to try and lift it from the conveyor up onto a stack. It is believed this occurs due to the weight of the sheet being too heavy to be supported by the wet interlaminar bond of the material because of the sheet thickness and high moisture content (approximately double the green sheet moisture content of normal fibre reinforced cement). Further, although the green sheet moisture content is higher than usual, it is possible that the green sheet is

in fact too dry leading to a weak wet bond between laminates.

**[0041]** This green sheet delamination may be avoided or at least reduced by inclusion of an additive eg bentonite 0.6% to increase the bond between the laminates.

**[0042]** The applicant has also developed several modifications to the Hatschek process to improve the green sheet properties. Apart from the conventional techniques of:

- 5 a) increasing the pre-curing time
- b) adding a load to the top of some stacks after forming and maintaining such a load until after autoclaving, and/or
- 10 c) modifying the autoclave cycle (pressurising and depressurising rates) the applicants have found that adding bleached pulp instead of unbleached pulp to the formulation improves the properties of the green sheet for subsequent processing.

**[0043]** Further, the applicant has found that narrow widths of sheets (around 300 mm or less) even at 18 mm thickness are easier to process than a full sheet.

**[0044]** Surprisingly, the abovementioned processing modification also greatly increased the ultimate tensile strength or inter-laminar bond perpendicular to the face of the sheet. This is shown in the accompanying graph. The curve shows the ILB (inter-laminar bond) achieved with sheet produced using standard formulation fibre cement with unbleached pulp, density modified by the addition of CSH. The shaded region of the graph demonstrates the typical ILB achieved with the abovementioned processing modifications. The abovementioned modifications more than doubled the ILB at densities of around 0.8-0,9 g/cm<sup>3</sup>.

**[0045]** In certain cases, it may also be desirable to treat autoclaved boards prepared in accordance with the invention with a silane, siloxane or another silicone treatment. While the surface water permeability of the building products produced by the inventive process is low as compared with conventional boards, such treatment may be necessary since the low density cement boards will have a large number of pores throughout. The silane, siloxane or other silicone treatment makes these pores hydrophobic thereby reducing water absorption and further lowering surface water permeability.

**[0046]** The applicant has found that the present inventive process provides building products with a surface water permeability of around 0.6 mL/hr (averaged over 48 hours) down to as low as 0.4 mL/hr whereas conventional boards have a surface permeability of around 0.8-1.9 mL/hr. Surface Water Permeability was measured by exposing a 50 mm diameter circular area of a 250 x 250 square sample to a 1.22m column of water at 23 ± 2°C for 48 hours and measuring the drop in the water level over the 48 hrs. The result is quoted as mL drop per hour.

**[0047]** The term "comprising" is used throughout the specification in an inclusive sense that is to say in the sense of "including but not limited to" or "containing but not limited to". The term is not intended in an inclusive sense ie "consisting only of" or "composed only of".

#### 35 MODES FOR CARRYING OUT THE INVENTION

**[0048]** The present invention will now be described with reference to the following examples which should be considered in all respects as illustrative and non-restrictive:

**[0049]** By way of explanation, the following terms are used throughout the examples.

**[0050]** Ordinary Portland cement - hydraulic binder consisting of calcium silicates, calcium aluminates and calcium aluminoferrites manufactured from Portland cement, clinker and gypsum. The binder may contain small quantities, usually less than 5% by mass, of limestone, fly ash, granulated slag or combinations of all three materials. Additives that alter setting time, water demand, drying shrinkage and other properties may also be contained.

**[0051]** Off-white Portland cement - hydraulic binder consisting of calcium silicates, calcium aluminates and calcium aluminoferrites manufactured from Portland cement, clinker and gypsum. The ferrite phases are minimised to below 4% to produce the off-white colour. This results in an increase in the silicate and aluminate phases. As with ordinary Portland cement, it may contain small quantities of other materials and additives to alter its properties.

**[0052]** Blended cement - hydraulic binder consisting of ordinary Portland cement and/or off-white cement and one or a combination of the following materials, limestone, granulated slag and condensed silica fume. The proportion of these additions in excess of 5% by mass. Additives that alter setting time, water demand, drying shrinkage and other properties may also be contained.

**[0053]** Fly ash - the fine material collected in electrostatic, mechanical filters or bag filters from boilers fired with pulverised fuels such as coal. Depending on the mineral types, fly ash can be pozzolanic with degree determined by the quantity and types of calcium silicates present. Fly ash is also known as pulverised fuel ash.

**[0054]** Slag - the material containing calcium, magnesium and other silicates, aluminates and aluminosilicates separated from smelting of metals such as iron, steel, copper, etc whilst in a molten state.

**[0055]** Iron blast furnace slag - a by-product separated from molten iron during manufacture of iron in an iron blast

furnace. The material consists of calcium and magnesium silicates, aluminates and aluminosilicates as well as other minerals in smaller quantities.

[0056] Steel slag - a by-product separated from molten steel during manufacture of steel and its alloys. The material consists of calcium and magnesium silicates, aluminates and aluminosilicates as well as other minerals in smaller quantities.

[0057] Granulated slag - a glass material obtained by quenching molten slag in air, water or a mixture of both. This process known as granulation produces mainly amorphous materials that possess latent hydraulic properties.

[0058] Crystalline or Air-cooled slag - when molten slags are allowed to cool slowly, crystalline minerals result and the slag does not show any significant hydraulic properties.

[0059] It will be appreciated from the above, therefore, that the cementitious material and siliceous material in the inventive formulation may be provided by a single source material eg a blended Portland cement. It may also be envisaged that the calcareous reactant and siliceous reactant may be provided by a single source material eg a siliceous limestone deposit.

**EXAMPLE 1 - Synthesis of Low Bulk Density Calcium Silicate Hydrate**

[0060] Process lime water is weighed into the batch tank at a ratio of 6.0L water per kg of lime (CaO) in the batch. It should be noted that the present inventive process is suitable for use with both fresh town water or process water. The water is discharged into the mixing tank and then heated with steam to 65°C. The steam adds extra water. A 1300 kg batch of raw materials requires 628 kg of lime which is slaked in 3767 Litres of lime water and 672 kg dry weight of ground quartz sand in a slurry at 40% solids which is added to the slaked lime in a stirred tank. The preparation of the silica sand is described below.

[0061] The quartz sand was ground in a vertical stirred ball mill to a particle size such that 90% the volume of silica is less than 11.60 micron (11.60  $\mu\text{m}$ ) diameter as measured by a Malvern "Mastersizer" laser diffraction particle size analyser.

[0062] The slurry is mixed for 15 minutes then pumped into the stirred pressure vessel. Water is added to modify the viscosity of the slurry. The slurry is heated with steam to a pressure of approximately  $700 \pm 50$  kPa. The reaction is maintained at this pressure by addition of steam into the vessel. The material is maintained at pressure for 3 hours by further intermittent injection of steam. After 3 hours at full pressure, the pressure is then reduced to approximately 270 kPa in 30 minutes. The material is then discharged into a tank via a cyclone to allow the liberation of steam from the slurry. The slurry is then diluted with lime water to between 10-12 wt % dry solids of calcium silicate hydrate product. The slurry is then pumped to a stirred storage tank.

**Properties of the Low Bulk Density Calcium Silicate Hydrate**

[0063] The properties of the calcium silicate hydrate as synthesised by the method described above are listed below.

PROPERTY	VALUE
% A.I.R.	3.9%
% Unreacted	7.5%
Tamped Dry Bulk Density (kg/m <sup>3</sup> )	$217 \pm 10$ kg/m <sup>3</sup>
Filtration Time (seconds)	$107 \pm 15$ seconds
DTA - Wollastonite conversion peak temperature	839°C

**Definitions**

**[0064]**

**% ACID INSOLUBLE RESIDUE (AIR)**

% AIR is a measure of the unreacted quartz silica in the calcium silicate hydrate product. The method involves grinding 2 grams of sample and making it into a paste with water and then diluting with water to 200 mL, then adding 25 mL of analytical reagent Hydrochloric acid 32% w/w, density 1.16 g/mL (1:1). The mixture is heated at 90°-95°C for 15 minutes and filtered through a No. 40 Whatman filter paper. The residue is washed with boiling water and boiling Na<sub>2</sub>CO<sub>3</sub> (50g/L). The residue and filter paper are then ignited at 900°-1000°C, cooled in a desiccator and the residue weighed. The residue mass expressed as a percentage of the initial sample mass is the

% AIR.

% UNREACTED

% Unreacted is calculated as the % A.I.R. divided by the % silica of the batched dry raw materials (SiO<sub>2</sub> and CaO).

## 5 TAMPED BULK DENSITY

[0065] The calcium silicate hydrate product was dried in an oven at 105°C. The dried cake was broken up using a mortar and pestle and passed through 250µm screens to remove lumps. Conglomerated material that failed to pass through the sieves was broken up by hand and sieved again. (100 ± 1 cm<sup>3</sup>) of the sieved sample was placed in a preweighed measuring cylinder. This cylinder was shaken on a vibrating table for 10 to 15 minutes with periodic stirring with a piece of wire. Once volume reduction ceased, the volume and mass were recorded. The mass of the sample divided by the volume of the sample, expressed in kg/m<sup>3</sup>, was recorded as the Tamped Bulk Density.

## 15 FILTRATION TIME

[0066] Filtration Time is a measure of time taken for a 1.00 Litre sample of slurry to drain the water through a 12.5 cm diameter Buchner funnel and Whatman grade 541 filter paper, at a slurry temperature of 25° ± 5°C under a vacuum of -60 kPa. The slurry shall be between 10 wt % and 12 wt % dry solids. The start time is when the slurry first covers the filter paper and the finish time is when the vacuum drops to -30 kPa as the filter cake shrinks or cracks.

## 20 DTA - WOLLASTONITE CONVERSION PEAK TEMPERATURE

[0067] Differential Thermal Analysis (DTA) is a method used to characterise calcium silicate hydrates. The test method involves heating approximately 30 mg of sample under nitrogen gas at a rate of 20° per minute from ambient to 1000°C. The difference in temperature between an empty reference sample holder and the sample is measured versus temperature. The tobermorite phase of calcium silicate hydrate is characterised by an exothermic conversion to wollastonite phase at temperatures between 824° and 840°C. Wollastonite conversion temperatures above 840° up to 900°C are more typical of a reaction that has not proceeded to the tobermorite phase.

30 EXAMPLE 2 - Cementitious Product using low bulk density CSH

[0068] The low bulk density calcium silicate hydrate made by the method of example 1 was then combined into a fibre cement matrix formed, via a Hatschek machine process, into a 10 mm flat sheet and autoclaved at 175°C (900 kPa sat. steam pressure) for 8 hours. The formulation and properties of the material are described below.

	35 FORMULATION	FORMULATION I	FORMULATION 2
	Bleached Pulp refined to 200 to 250 mL csf freeness	11.0%	11.0%
	Off-White Cement (~ 400 m <sup>2</sup> /kg)	39.2%	41.0%
	Silica (350 - 380 m <sup>2</sup> /kg)	39.2%	27.4%
	Low Bulk Density Calcium Silicate Hydrate (example 1)	10.0%	20.0%
	Bentonite	0.6%	0.6%

## 45 FLAT SHEET MATERIAL PROPERTIES

[0069]

50 PROPERTY	FORMULATION 1	FORMULATION 2
3-POINT FLEXURAL TEST		
Density - OD (g/cm <sup>3</sup> )	0.87	0.79
Density - sat (g/cm <sup>3</sup> )	1.45	1.39
MOR ave - OD (MPa)	14.57	11.63
MOR ave - sat (MPa)	9.26	7.54

(continued)

PROPERTY	FORMULATION 1	FORMULATION 2
5 MOE - OD (GPa)	3.55	2.62
MOE - sat - (GPa)	2.21	1.52
Toughness-OD (kJ/m <sup>3</sup> )	3.95	4.3
Toughness -sat (kJ/m <sup>3</sup> )	16.83	14.05
10 TENSILE TEST of interlaminar bond		
ILB - (MPa)	1.51	1.48
MOR ave = Average Modulus of Rupture of test breaks in perpendicular directions		
MOE = Modulus of Elasticity		
OD = Tested in an oven dry condition (24 hrs @ 105°C)		
sat = Tested in a saturated condition (24 hrs submersion)		
ILB = ultimate tensile strength of the specimen (Inter-Laminar Bond tested perpendicular to the face of the sheet (44 mm x 44 mm sample size).		

20 EXAMPLE 3 - Synthesis of Low Bulk Density Calcium Silicate Hydrate

**[0070]** The example below demonstrates the art of converting lime and ground quartz silica to CSH of predominantly tobermorite phase within the short reaction time of only 2 hours with no greater than 10% Unreacted.

**[0071]** Silica sand of average particle size between 0.3 and 0.5 mm was ground in a vertical stirred ball mill. Silica was milled to a particle size of D[90] = 8.84µm. The D[90] value represents the particle size diameter that 90% of the weight of silica is less than, as measured by a 'Mastersizer' particle size analyser.

**[0072]** The lime and the milled silica were then mixed into an aqueous slurry and reacted in a stirred pressure vessel. The molar ratio of lime to silica was 1:1 and water was added to give a dry solids concentration of 4% ± 1%. The reaction was heated from ambient to 170° ± 5°C and a steam pressure of 750 ± 50 kPa in 40 minutes in the stirred pressure vessel and maintained at these conditions for 2.0 hours.

**[0073]** The extent of the reaction was measured by the acid insoluble residue test.

## Properties of the Low Bulk Density Calcium Silicate Hydrate

35 **[0074]** The properties of the calcium silicate hydrate as synthesised by the method described above are listed below.

PROPERTY	CSH made from 60 minute milled silica
Silica Particle size D[90]	8.84µm
% A.I.R.	2.1%
% Unreacted	4.1%
Tamped Dry Bulk Density (kg/m <sup>3</sup> )	84 ± 4 kg/m <sup>3</sup> *
DTA - Wollastonite conversion peak temperature	840°C

45 \* The tamped dry bulk density of the calcium silicate hydrate resulting from Example 3 is much lower than Example 1 for several reasons including:

50 (i) Example 1 was a full-scale production in large 9 m<sup>3</sup> reactors whereas Example 3 is a small lab scale experiment using reactor vessels of only about 3-4 litres,

(ii) the silica particle size in Example 3 is much finer than the silica particle size in Example 1, and

(iii) the percent solids concentration in Example 3 is much lower than Example 1.

EXAMPLE 4 - Cementitious Product using low bulk density CSH, fibre reinforcement and aeration

55 **[0075]** The density achievable by addition of low bulk density calcium silicate hydrate to cementitious and a fibre cement matrix are described in this example.

RAW MATERIALS	FORMULATION 1 %	FORMULATION 2 %
Cellulose Pinus Radiatus unbleached pulp (refined to 400 to 450 ml csf freeness)	11.25	0
Portland Type A cement (320 to 350 m <sup>2</sup> /kg)	14.82	30
Ground Quartz Sand (340 to 360 m <sup>2</sup> /kg)	22.24	30
Calcium Silicate Hydrate (as described in eg 1)	50.00	39
Aluminium Powder	0	1
Metal Hydroxide	1.69	0

[0076] Formulation 1 was manufactured by mixing and pressing a slurry of 3:1 water to solids between two meshes to dewater the slurry and form a monolithic sheet material. The sheet was then steam autoclaved at 175°C for 8 hours.

[0077] Formulation 2 was manufactured by mixing the ingredients in a mass ratio of 3:1 water to solids and then autoclaving same as formulation 1. The 1% aluminium powder was added to supply aeration to the slurry via reaction to produce hydrogen and further lower the density and then autoclaved.

[0078] The resultant fibre reinforced cement products had the following properties

PROPERTIES (Oven Dried 105°C for 24 hrs)	FORMULATION 1	FORMULATION 2
Dry Density (g/cm <sup>3</sup> )	0.587 ± 0.019	0.24 ± 0.02
MoR ave. (MPa)	4.82 ± 0.39	
MoE (GPa)	0.94 ± 0.19	
Toughness (kJ/m <sup>3</sup> )	2.69 ± 0.42	
Thickness (mm)	15.06 ± 0.45	

#### EXAMPLE 5 - Silane Treatment

[0079] An undesirable property of fibre cement is the capillary rise of water up through the material when the lower edges are immersed in or saturated by water. The phenomenon is also commonly known as wicking. The hydrophilic nature of the cementitious pores induces the capillary action of water.

[0080] It was hypothesised that if the surface properties of the pores could be modified to produce a hydrophobic pore surface, the capillary rise of water could be reduced or stopped. A silane chemical was selected because of its ability to react with the hydroxyl groups at the pore surfaces and its hydrophobic nature of the tail of the molecule.

[0081] A silane supplied by Wacker Chemicals (GF 31) was selected to test the hypothesis. Methacryloxypropyltrimethoxysilane, was used to treat Low Density Cementitious Board prepared in accordance with the present invention to reduce the rate at which water wicks through the board. This silane was chosen because it also bonds well with acrylics that are the most common binder in current paint coatings for fibre reinforced cement products.

[0082] The silane was prepared by hydrolysing 20g of silane in 2L of 2 wt % acetic acid solution for 15 minutes. Two pre-dried low density board samples (250 mm x 250 mm x 10 mm) were soaked in the solution for 30 minutes, removed and dried at 105°C for 12 hours. The samples were tested for wicking and water permeability and the results compared with a sample of untreated board.

[0083] Wicking testing involved constant immersion of the bottom 25 mm of the sample in clean tap water, and measurement of the height to which the water was drawn up in the middle of the sample over time.

[0084] Surface Water Permeability was measured by exposing a 50 mm diameter circular area of a 250 x 250 square sample to a 1.22m column of water at 23 ± 2°C for 48 hours and measuring the drop in the water level over the 48 hrs. The result is quoted as mL drop per hour.

[0085] The results of the wicking test are indicated in the following table.

Wicking Results		
TIME OF IMMERSION	Wicking Height (mm) Untreated Board	Wicking Height (mm) Sliane Treated Board
35 minutes	9	0

(continued)

Wicking Results			
	TIME OF IMMERSION	Wicking Height (mm) Untreated Board	Wicking Height (mm) Silane Treated Board
5	75 minutes	9	0
	2.5 hours	10	0
	5 hours	12	0
10	7 hours	15	0
	3 days	40	1
	5 days	45	2
15	7 days	51	3

Surface Water Permeability Results			
	SAMPLE	PERMEABILITY (mL/hour)	
20	Untreated	0.59	
25	Silane Treated	0.21	

**[0086]** The results show that the silane treatment dramatically slowed or even prevented wicking, and that the surface water permeability of the board was substantially reduced.

**EXAMPLE 6 (Comparison) - Injection Molded Cementitious Product using Low Bulk Density Calcium Silicate Hydrate (CSH)**

**[0087]** The low bulk density CSH of a grade called "Microcel E" supplied by Celite Corporation was combined into fibre cement formulations and formed into a green shaped product via an injection moulding process. The moulded green product was then pre-cured for 8 to 12 hours then autoclaved as in Example 2. The properties of the "Microcel E", the formulation and the autoclaved material properties are shown in the table below:

PROPERTIES OF "MICROCEL E"	
Tamped Bulk Density (kg/m <sup>3</sup> )	170
Filtration time (seconds)	approximately 110

FORMULATION Raw Materials	FORMULATION 1 (wt %)	FORMULATION 2 (wt %)
Unbleached Kraft Pinus Radiata Fibre refined to 400-450 CSF	11	0
Bleached Kraft Pinus Radiata Fibre refined to 400-450 CSF	0	11
Shrinkage Limited Ordinary Portland Cement (335 m <sup>2</sup> /kg)	41	32
Silica (360m <sup>2</sup> /kg)	28	22
Low Bulk Density Calcium Silicate Hydrate (Microcel E)	20	35

**[0088]** The formulations above were mixed with process water to achieve slurry mixtures of a weight percent solids approximately equal to 12% to 17% prior to injection into moulds and press de-watering operations.

Flat Sheet Material Properties

[0089] material was cut from a flat section of the moulded and autoclaved product. The thickness of the test sample was approximately 8 mm.

FORMULATION 1		
PROPERTY	OVEN DRY (105°C, 24 hours)	WATER SATURATED.
Density (g/cm <sup>3</sup> )	0.93	1.63
M.O.R. a (MPa)	6.19	1.63
M.O.E. a (GPa)	0.77	0.61
Energy to fracture (kJ/m <sup>3</sup> )	3.77	1.86

M.O.R. a = Modulus of Rupture using a single break per sample  
M.O.E. a = Modulus of Elasticity using single break per sample

FORMULATION 2 Dry Density = 0.82 g/cm <sup>3</sup>		
PROPERTY	WATER SATURATED	
M.O.R. a (MPa)	5.61	

EXAMPLE 7 - Cementitious Product using Low Bulk Density Calcium Silicate Hydrate (CSH) and Blended Cement

[0090] A low bulk density calcium silicate hydrate was made by reacting 674 kg of ground silica (90 wt % < 28.7 µm), 326 kg of lime and 5400 L of water for 2 hours at 175°C in a stirred pressure vessel. This material was then combined with fibres into cementitious matrices to form flat sheets. Fibre reinforced cement sheets were produced using three formulations. The sheets were made by mixing the following materials to form a slurry, then pressing the slurry between fine sieve mesh to form a sheet material of 12 mm thickness. The sheets were autoclaved at 173°C (860 kPa sat, steam pressure) for 5 hours. The formulations and properties of the material are described below:

Raw Material	Formulation 1	Formulation 2	Formulation 3
Bleached Kraft Pinus Radiata Fibre refined to 400-450 CSF	11.0	11.0	11.0
Shrinkage Limited Ordinary Portland Cement (335 m <sup>2</sup> /kg)	41.4	0	0
Silica (360 m <sup>2</sup> /kg)	27.6	0	27.6
Low Bulk Density Calcium Silicate Hydrate	20.0	20.0	20.0
Builders Cement (containing 40% Ground Granulated Blast furnace slag) (400 m <sup>2</sup> /kg)	0	69.0	0
Marine Cement (Containing 60% Ground Granulated Blast Furnace Slag) (420 m <sup>2</sup> /kg)	0	0	41.4

FLAT SHEET MATERIALS PROPERTIES			
Properties	Formulation 1	Formulation 2	Formulation 3
3 POINT FLEXURAL TEST After drying at 70°C and 30% Relative Humidity			
Density (g/cm <sup>3</sup> )	0.967	0.964	0.920
M.O.R. ave (MPa)	12.9	10.0	11.6
M.O.E. (GPa)	3.75	2.40	2.98
Ultimate Strain (µm/m)	3760	5470	4820
Energy to Fracture (kJ/m <sup>3</sup> )	3.03	3.88	3.73

(continued)

FLAT SHEET MATERIALS PROPERTIES				
Properties	Formulation 1	Formulation 2	Formulation 3	
3 POINT FLEXURAL TEST After drying at 70°C and 30% Relative Humidity				
M.O.R. ave = Average Modulus of Rupture of test breaks in perpendicular directions				
M.O.E. = Modulus of Elasticity				
Ultimate strain = Strain at maximum load				

## EXAMPLE 8 - Cementitious Product using Commercially Available Low Density Calcium Silicate Hydrate

[0091] A low bulk density calcium silicate hydrate sold under the trade name "Silasorb" by Celite Corporation was combined into a fibre cement matrix by a Hatschek machine process. Sheets of 11 mm thickness were autoclaved at 175°C (900 kPa) saturated steam pressure) for 8 hours. The formulation and properties of the materials are shown below:

PROPERTIES OF SILASORB	
Tamped Bulk Density (kg/m <sup>3</sup> )	260
Filtration Time (seconds)	45-60

FORMULATION	
Raw Material	Formulation (wt %)
Bleached Kraft Pinus Radiata Fibre refined to 400-450 CSF	11
Shrinkage Limited Ordinary Portland Cement 335 m <sup>2</sup> /kg)	41
Silica (360 m <sup>2</sup> /kg)	28
Low Bulk Density Calcium Silicate Hydrate	20

FLAT SHEET MATERIAL PROPERTIES				
Property	Oven Dry (105°C, 24 hours)	Equilibrium (25°C and 50% R.H.)	Water Saturated	
Density (g/cm <sup>3</sup> )	0.87	0.90	1.46	
M.O.R. a (MPa)	12.54	12.7	6.73	
M.O.E. a (GPa)	3.28	2.91	1.39	
Energy to Fracture (kJ/m <sup>3</sup> )	3.25	8.53	14.79	
M.O.R. a = Modulus of Rupture using single break per sample				
M.O.E. a - Modulus of Elasticity using single break per sample				

[0092] The calcium silicate hydrate of the present invention is suitable for the production of cementitious products for both internal and external applications.

[0093] The present invention provides a general purpose low density fibre cement building material which is suitable for use in a wide range of applications. The present invention provides the ability to make thick fibre cement sheets while maintaining ease of nailing. This property provides new opportunities for development of specialised products such as timber trim replacement, siding, fascias, roofing, eave sheets and components thereof on external surfaces of buildings. Further, the inventive process is particularly well suited to the Hatschek process because the CSH material described unlike other common density modifiers such as vermiculite and perlite, does not float and resists crushing. These characteristics together with its ease of dewatering and other features described above enable high production rates on the Hatschek machine.

[0094] Although the invention has been described with reference to selected examples, it will be appreciated by

those skilled in the art that the invention may be embodied in many other forms.

**Claims**

- 5 1. A method for forming a cementitious product comprising adding a cementitious material, a siliceous material and a low bulk density material to water to form a slurry forming a green shaped article from the slurry and curing the article in an autoclave,  
**characterised in that** the low bulk density material is a mixture of calcium silicate hydrate and unreacted siliceous reactant.
- 10 2. A method as claimed in claim 1 wherein the low bulk density material has a bulk density between 0.06 and 0.3 g/cm<sup>3</sup>.
- 15 3. A method as claimed in claim 1 or claim 2 wherein the low bulk density material is provided by reacting a siliceous reactant with a calcareous reactant in the presence of water under pressure and elevated temperature, wherein at least 90 wt % of the siliceous reactant has a particle size of less than 100 microns (100 µm).
- 20 4. A method as claimed in any one of the preceding claims wherein fibrous and/or other additives are added to the slurry prior to the formation of the green shaped article.
- 25 5. A method as claimed in any one of the preceding claims wherein the green shaped article is formed by the Hatschek process.
- 30 6. A method as claimed in any one of the preceding claims wherein the green shaped article is formed by filter process.
- 35 7. A method as claimed in any one of the preceding claims wherein the green shaped article is formed by injection moulding.
- 40 8. A method as claimed in any one of the preceding claims wherein the green shaped article is formed by extrusion.
- 30 9. A method as claimed in any one of claims 3-8 wherein the reaction is terminated prior to complete conversion of the reactants to calcium silicate hydrate.
- 45 10. A method as claimed in any one of claims 3-9 wherein the reaction is conducted for less than 4 hours.
- 35 11. A method as claimed in any one of claims 3-10 wherein the reaction is conducted over a period of up to 2 hours with at least 80% of the calcareous reactant material being converted to calcium silicate hydrate.
- 40 12. A method as claimed in any one of claims 3-11 wherein prior to or during the reaction, water is added in an amount of up to 30 times the total weight of the siliceous and calcareous reactants.
- 45 13. A method as claimed in any one of claims 3-12 wherein the reaction is conducted at a temperature of between 120 and 250 °C.
- 50 14. A method as claimed in any one of claims 3-13 wherein the reaction is conducted at a temperature of between 160 and 180°C.
- 55 15. A method as claimed in any one of claims 3-14 wherein the reaction is conducted at a pressure of between 200 and 4000 kPa.
16. A method as claimed in any one of claims 3-15 wherein the reaction is conducted at a pressure between 600 and 1000 kPa.
17. A method as claimed in any one of claims 3-16 wherein the calcareous reactant and siliceous reactant are reacted in a molar ratio of CaO:SiO<sub>2</sub> between 0.1 and 1.2.
18. A method as claimed in any one of claims 3-17 wherein the calcareous reactant and siliceous reactant are reacted in a molar ratio of CaO:SiO<sub>2</sub> between 0.3 and 0.8.

19. A method as claimed in any one of claims 3-18 wherein the siliceous reactant has a particle size of 90 wt % less than 70 microns (70  $\mu\text{m}$ ).

20. A method as claimed in any one of claims 3-19 wherein the siliceous reactant has a particle size of 90 wt % less than 50 microns (50  $\mu\text{m}$ ).

21. A method as claimed in any one of the preceding claims wherein the siliceous reactant and/or siliceous material is amorphous.

22. A method as claimed in any one of the preceding claims wherein the siliceous reactant and/or siliceous material is crystalline.

23. A method as claimed in any one of claims 3-22 wherein the calcareous reactant is lime.

24. A method as claimed in any one of claims 3-23 wherein the calcareous reactant is quick lime.

25. A method as claimed in any one of claims 3-24 wherein the calcareous reactant contains greater than 90% CaO.

26. A method as claimed in any one of the preceding claims wherein the siliceous reactant and/or siliceous material is selected from the group consisting of silica, quartz, quartz rock, quartzite sand, diatomaceous earth, silica fume, rice hull ash, fly ash, blast furnace slag, granulated slag, steel slag, crystalline or air cooled slag, geothermal silica and mixtures thereof.

27. A method as claimed in any one of claims 3-26 wherein the siliceous reactant and the calcareous reactant originate from a single source material.

28. A method as claimed in any one of claims 3-26 wherein the siliceous reactant and the calcareous reactant originate from separate source materials.

29. A method as claimed in any one of the preceding claims wherein the cementitious material is selected from the group consisting of cement, lime, lime-containing material, Portland cement, off-white cement, blended cement, hydrated lime or mixtures thereof.

30. A method as claimed in any one of the preceding claims wherein the cementitious material and the siliceous material originate from a single source material.

31. A method as claimed in any one of the preceding claims wherein the cementitious material and the siliceous material originate from separate source materials.

32. A method as claimed in any one of the preceding claims wherein the cementitious product is treated with silane, siloxane and/or silicone to reduce its water absorption and surface water permeability characteristics.

33. A method as claimed in any one of the preceding claims wherein the low bulk density material is added in sufficient quantities such that the resultant cementitious product has a density between 0.5 and 12 g/cm<sup>3</sup>.

34. A formulation for preparing a cementitious product comprising:

50 a cementitious material  
a siliceous material, and  
a low bulk density material,

characterised in that the low bulk density material is a mixture of calcium silicate hydrate and unreacted siliceous reactant.

35. A formulation as claimed in claim 34 wherein the low bulk density material has a bulk density of between 0.06 and 0.3 g/cm<sup>3</sup>.

36. A formulation as claimed in claim 34 wherein the low bulk density material is produced by reacting a siliceous

reactant with a calcareous reactant in the presence of water under pressure and elevated temperature to form the low bulk density material, at least 90 wt % of the siliceous reactant having a particle size of less than 100 microns (100  $\mu\text{m}$ ).

- 5 37. A formulation as claimed in any one of claims 34-36 further including water.
38. A formulation as claimed in any one of claims 34-37 wherein the low bulk density material is added in an amount up to 80% by weight of dry ingredients.
- 10 39. A formulation as claimed in any one of claims 34-38 wherein the low bulk density material is added in an amount up to 50% by weight of dry ingredients.
40. A formulation as claimed in any one of claims 34-39 wherein the low bulk density material is added in sufficient quantities that the resultant cementitious product has a density between 0.5 and 1.2 g/cm<sup>3</sup>.
- 15 41. A formulation as claimed in any of claims 34-40 wherein the amount of siliceous material is between 10 and 80% by weight of dry ingredients.
- 20 42. A formulation as claimed in any one of claims 34-41 wherein the amount of siliceous material is between 40 and 65% by weight of dry ingredients.
- 25 43. A formulation as claimed in any one of claims 34-42 wherein the siliceous reactant and/or siliceous material is selected from the group consisting of silica, quartz, quartz rock, quartzite sand, diatomaceous earth, silica fume, rice hull ash, fly ash, blast furnace slag, granulated slag, steel slag, crystalline or air-cooled slag, geothermal silica and mixtures thereof.
44. A formulation as claimed in any one of claims 34-43 wherein the siliceous reactant and/or the siliceous material is amorphous.
- 30 45. A formulation as claimed in any one of claims 34-43 wherein the siliceous reactant and/or the siliceous material is crystalline.
46. A formulation as claimed in any one of claims 34-45 wherein the amount of cementitious material is between 10 and 80% by weight of dry ingredients.
- 35 47. A formulation as claimed in any one of claims 34-46 wherein the amount of cementitious material is between 30 and 40% by weight of dry ingredients.
48. A formulation as claimed in any one of claims 34-47 wherein the cementitious material is selected from the group consisting of cement, lime, lime-containing material, Portland cement, off-white cement, blended cement, hydrated lime or mixtures thereof.
- 40 49. A formulation as claimed in any one of claims 34-48 wherein the siliceous material and the cementitious material originate from a single source material.
- 50 50. A formulation as claimed in any one of claims 34-48 wherein the siliceous material and the cementitious material originate from separate source materials.
51. A formulation as claimed in any one of claims 36-50 wherein the calcareous reactant is lime.
52. A formulation as claimed in any one of claims 36-51 wherein the calcareous reactant is quick lime.
53. A formulation as claimed in any one of claims 36-52 wherein the calcareous reactant contains greater than 90% CaO.
- 55 54. A formulation as claimed in any one of claims 36-53 wherein the siliceous reactant and the calcareous reactant originate from a single source material.

55. A formulation as claimed in any one of claims 36-53 wherein the siliceous reactant and the calcareous reactant originate from separate source materials.

56. A formulation as claimed in any one of claims 34-55 further including 0-25% by weight of dry ingredients, of an asbestos fibre material.

57. A formulation as claimed in any one of claims 34-55 further including 0-25% by weight of dry ingredients, of a non-asbestos fibrous material selected from the group consisting of cellulose wood fibres, non-wood cellulose fibres, mineral wool, steel fibres, synthetic polymer fibres such as polyamides, polyesters, polypropylene, polymethylpentene, polyacrylonitrile, polyacrylamide, viscose, nylon, PVC, PVA, rayon and glass, ceramic or carbon and mixtures thereof.

10 58. A formulation as claimed in claim 57 wherein the fibres are cellulose fibres which are bleached, unbleached, partially bleached or mixtures thereof.

15 59. A formulation as claimed in any one of claims 56-58 wherein the amount of fibrous material is between 2 and 15% by weight of dry ingredients.

20 60. A formulation as claimed in any one of claims 56-59 wherein the amount of fibrous material is between 5 and 14% by weight of dry ingredients.

25 61. A formulation as claimed in any one of claims 34-60 further including 0-40% by weight of dry ingredients, of other additives selected from the group consisting of fillers, fire retardants, thickeners, colorants, pigments, water sealing agents, water reducing agents, water retaining agents, setting rate modifiers, hardeners, filler aids, plasticisers, dispersants, foaming agents, defoaming agents, flocculating agents, waterproofing agents, density modifiers and mixtures thereof.

30 62. A formulation as claimed in any one of claims 34-61 further including 0-40% by weight of dry ingredients, of other additives selected from the group consisting of mineral oxides, mineral hydroxides and clays, metal oxides and hydroxides, magnesite, dolomite, aluminium powder, alumina trihydrate, kaolin, mica, metakaolin, silica fume, calcium carbonate, wollastonite, methyl cellulose and mixtures thereof.

35 63. A cementitious product comprising the autoclave cured reaction product of the formulation as claimed in any one of claims 34-62.

#### Patentansprüche

1. Verfahren zum Bilden eines zementösen Produkts, wobei ein zementöses Material, ein silikatisches Material und ein Material niedriger Schüttdichte zu Wasser hinzugefügt werden, um eine Aufschlämmung zu bilden, ein geformter Rohartikel aus der Aufschlämmung gebildet wird und der Artikel in einem Autoklaven gehärtet wird, dadurch gekennzeichnet, dass das Material niedriger Schüttdichte eine Mischung aus Calciumsilikathydrat und nicht in Reaktion getretenem silikatischen Reaktionspartner ist.

40 2. Verfahren nach Anspruch 1, wobei das Material niedriger Schüttdichte eine Schüttdichte zwischen 0,06 und 0,3 g/cm<sup>3</sup> hat.

3. Verfahren nach Anspruch 1 oder 2, wobei das Material niedriger Schüttdichte bereitgestellt wird durch Reagieren eines silikatischen Reaktionspartners mit einem kalkartigen Reaktionspartner in Gegenwart von Wasser unter Druck und erhöhter Temperatur, wobei wenigstens 90 Gew.-% des silikatischen Reaktionspartners eine Teilchengröße von weniger als 100 Mikron (100 µm) hat.

45 4. Verfahren nach einem der vorhergehenden Ansprüche, wobei vor der Bildung des geformten Rohartikels faserige und/oder andere Zusätze zu der Aufschlämmung hinzugefügt werden.

50 5. Verfahren nach einem der vorhergehenden Ansprüche, wobei der geformte Rohartikel durch den Hatschek-Prozess gebildet wird.

6. Verfahren nach einem der vorhergehenden Ansprüche, wobei der geformte Rohartikel durch einen Filterprozess gebildet wird.
7. Verfahren nach einem der vorhergehenden Ansprüche, wobei der geformte Rohartikel durch Spritzgießen gebildet wird.
8. Verfahren nach einem der vorhergehenden Ansprüche, wobei der geformte Rohartikel durch Extrusion gebildet wird.
9. Verfahren nach einem der Ansprüche 3 bis 8, wobei die Reaktion vor der vollständigen Umwandlung der Reaktionspartner zu Calciumsilikathydrat beendet wird.
10. Verfahren nach einem der Ansprüche 3 bis 9, wobei die Reaktion für weniger als 4 Stunden durchgeführt wird.
11. Verfahren nach einem der Ansprüche 3 bis 10, wobei die Reaktion über eine Periode von bis zu 2 Stunden durchgeführt wird, wobei wenigstens 80 % des kalkartigen Reaktionspartnermaterials zu Calciumsilikathydrat umgewandelt werden.
12. Verfahren nach einem der Ansprüche 3 bis 11, wobei vor oder während der Reaktion Wasser in einer Menge von bis zu 30 mal dem Gesamtgewicht der silikatischen und kalkartigen Reaktionspartner hinzugefügt wird.
13. Verfahren nach einem der Ansprüche 3 bis 12, wobei die Reaktion bei einer Temperatur zwischen 120 und 250 °C durchgeführt wird.
14. Verfahren nach einem der Ansprüche 3 bis 13, wobei die Reaktion bei einer Temperatur zwischen 160 und 180 °C durchgeführt wird.
15. Verfahren nach einem der Ansprüche 3 bis 14, wobei die Reaktion bei einem Druck zwischen 200 und 4000 kPa durchgeführt wird.
16. Verfahren nach einem der Ansprüche 3 bis 15, wobei die Reaktion bei einem Druck zwischen 600 und 1000 kPa durchgeführt wird.
17. Verfahren nach einem der Ansprüche 3 bis 16, wobei der kalkartige Reaktionspartner und der silikatische Reaktionspartner in einem molaren Verhältnis von CaO:SiO<sub>2</sub> zwischen 0,1 und 1,2 miteinander reagiert werden.
18. Verfahren nach einem der Ansprüche 3 bis 17, wobei der kalkartige Reaktionspartner und der silikatische Reaktionspartner in einem molaren Verhältnis von CaO:SiO<sub>2</sub> zwischen 0,3 und 0,8 miteinander reagiert werden.
19. Verfahren nach einem der Ansprüche 3 bis 18, wobei der silikatische Reaktionspartner bei 90 Gew.-% eine Teilchengröße von weniger als 70 Mikron (70 µm) hat.
20. Verfahren nach einem der Ansprüche 3 bis 19, wobei der silikatische Reaktionspartner bei 90 Gew.-% eine Teilchengröße von weniger als 50 Mikron (50 µm) hat.
21. Verfahren nach einem der vorhergehenden Ansprüche, wobei der silikatische Reaktionspartner und/oder das silikatische Material amorph ist.
22. Verfahren nach einem der vorhergehenden Ansprüche, wobei der silikatische Reaktionspartner und/oder das silikatische Material kristallin ist.
23. Verfahren nach einem der Ansprüche 3 bis 22, wobei der kalkartige Reaktionspartner Kalk ist.
24. Verfahren nach einem der Ansprüche 3 bis 23, wobei der kalkartige Reaktionspartner Ätzkalk ist.
25. Verfahren nach einem der Ansprüche 3 bis 24, wobei der kalkartige Reaktionspartner mehr als 90 % CaO enthält.
26. Verfahren nach einem der vorhergehenden Ansprüche, wobei der silikatische Reaktionspartner und/oder das si-

silikatische Material ausgewählt ist aus der Gruppe, die aus Siliciumdioxid, Quarz, Quarzit, Quarzsand, Kieselgur, Quarzstaub, Reishülsenrasche, Flugasche, Hochofenschlacke, granulierter Schlacke, Stahlschlacke, kristalliner oder luftgekühlter Schlacke, geothermischem Silikatmaterial und Mischungen davon besteht.

5      27. Verfahren nach einem der Ansprüche 3 bis 26, wobei der silikatische Reaktionspartner und der kalkartige Reaktionspartner von einem einzigen Ausgangsmaterial stammen.

10     28. Verfahren nach einem der Ansprüche 3 bis 26, wobei der silikatische Reaktionspartner und der kalkartige Reaktionspartner von verschiedenen Ausgangsmaterialien stammen.

15     29. Verfahren nach einem der vorhergehenden Ansprüche, wobei das zementöse Material ausgewählt ist aus der Gruppe, die aus Zement, Kalk, kalkhaltigem Material, Portlandzement, nichtweißem Zement, gemischtem Zement, hydrierter Kalk oder Mischungen davon besteht.

20     30. Verfahren nach einem der vorhergehenden Ansprüche, wobei das zementöse Material und das silikatische Material von einem einzigen Ausgangsmaterial stammen.

25     31. Verfahren nach einem der vorhergehenden Ansprüche, wobei das zementöse Material und das silikatische Material von verschiedenen Ausgangsmaterialien stammen.

30     32. Verfahren nach einem der vorhergehenden Ansprüche, wobei das zementöse Produkt mit Silan, Siloxan und/oder Silikon behandelt wird, um seine Wasserabsorption und Oberflächenwasser-Durchlässigkeitseigenschaften zu reduzieren.

35     33. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Material niedriger Schüttdichte in ausreichenden Mengen hinzugefügt wird, so dass das resultierende zementöse Produkt eine Dichte zwischen 0,5 und 1,2 g/cm<sup>3</sup> hat.

40     34. Formulierung zum Zubereiten eines zementösen Produkts, mit:

45     einem zementösen Material,  
      einem silikatischen Material, und  
      einem Material niedriger Schüttdichte,

50     dadurch gekennzeichnet, dass das Material niedriger Schüttdichte eine Mischung aus Calciumsilikathydrat und nicht in Reaktion getretenem silikatischen Reaktionspartner ist.

55     35. Formulierung nach Anspruch 34, wobei das Material niedriger Schüttdichte eine Schüttdichte zwischen 0,06 und 0,3 g/cm<sup>3</sup> hat.

60     36. Formulierung nach Anspruch 34, wobei das Material niedriger Schüttdichte durch Reaktion eines silikatischen Reaktionspartners mit einem kalkartigen Reaktionspartner in Gegenwart von Wasser unter Druck und erhöhter Temperatur hergestellt ist, um das Material niedriger Schüttdichte zu bilden, wobei wenigstens 90 Gew.-% des silikatischen Reaktionspartners eine Teilchengröße von weniger als 100 Mikron (100 µm) haben.

65     37. Formulierung nach einem der Ansprüche 34 bis 36, die ferner Wasser enthält.

70     38. Formulierung nach einem der Ansprüche 34 bis 37, wobei das Material niedriger Schüttdichte in einer Menge bis zu 80 Gew.-% trockener Zutaten hinzugefügt wird.

75     39. Formulierung nach einem der Ansprüche 34 bis 38, wobei das Material niedriger Schüttdichte in einer Menge bis zu 50 Gew.-% trockener Zutaten hinzugefügt wird.

80     40. Formulierung nach einem der Ansprüche 34 bis 39, wobei das Material niedriger Schüttdichte in ausreichenden Mengen hinzugefügt wird, so dass das resultierende zementöse Produkt eine Dichte zwischen 0,5 und 1,2 g/cm<sup>3</sup> hat.

85     41. Formulierung nach einem der Ansprüche 34 bis 40, wobei die Menge des silikatischen Materials zwischen 10 und

80 Gew.-% trockener Zutaten liegt.

42. Formulierung nach einem der Ansprüche 34 bis 41, wobei die Menge an silikatischem Material zwischen 40 und 65 Gew.-% trockener Zutaten liegt.

5 43. Formulierung nach einem der Ansprüche 34 bis 42, wobei der silikatische Reaktionspartner und/oder das silikatische Material aus der Gruppe ausgewählt ist, die aus Siliciumdioxid, Quarz, Quarzit, Quarzsand, Kieselgur, Quarzstaub, Reishülsenäsche, Flugasche, Hochofenschlacke, granulierter Schlacke, Stahlschlacke, kristalliner oder luftgekühlter Schlacke, geothermischem Silikatmaterial und Mischungen davon besteht.

10 44. Formulierung nach einem der Ansprüche 34 bis 43, wobei der silikatische Reaktionspartner und/oder das silikatische Material amorph ist.

15 45. Formulierung nach einem der Ansprüche 34 bis 43, wobei der silikatische Reaktionspartner und/oder das silikatische Material kristallin ist.

46. Formulierung nach einem der Ansprüche 34 bis 45, wobei die Menge an zementösem Material zwischen 10 und 80 Gew.-% trockener Zutaten liegt.

20 47. Formulierung nach einem der Ansprüche 34 bis 46, wobei die Menge an zementösem Material zwischen 30 und 40 Gew.-% trockener Zutaten liegt.

25 48. Formulierung nach einem der Ansprüche 34 bis 47, wobei das zementöse Material ausgewählt ist aus der Gruppe, die aus Zement, Kalk, kalkhaltigem Material, Portlandzement, nicht weißem Zement, gemischtem Zement, hydriertem Kalk oder Mischungen davon besteht.

49. Formulierung nach einem der Ansprüche 34 bis 48, wobei das silikatische Material und das zementöse Material von einem einzigen Ausgangsmaterial stammen.

30 50. Formulierung nach einem der Ansprüche 34 bis 48, wobei das silikatische Material und das zementöse Material von verschiedenen Ausgangsmaterialien stammen.

51. Formulierung nach einem der Ansprüche 36 bis 50, wobei der kalkartige Reaktionspartner Kalk ist.

35 52. Formulierung nach einem der Ansprüche 36 bis 51, wobei der kalkartige Reaktionspartner Ätzkalk ist.

53. Formulierung nach einem der Ansprüche 36 bis 52, wobei der kalkartige Reaktionspartner mehr als 90 % CaO enthält.

40 54. Formulierung nach einem der Ansprüche 36 bis 53, wobei der silikatische Reaktionspartner und der kalkartige Reaktionspartner von einem einzigen Ausgangsmaterial stammen.

55. Formulierung nach einem der Ansprüche 36 bis 53, wobei der silikatische Reaktionspartner und der kalkartige Reaktionspartner von verschiedenen Ausgangsmaterialien stammen.

45 56. Formulierung nach einem der Ansprüche 34 bis 55, die ferner 0 bis 25 Gew.-% trockener Zutaten an Asbestfasermaterial enthält.

50 57. Formulierung nach einem der Ansprüche 34 bis 55, die ferner 0 bis 25 Gew.-% trockener Zutaten an nicht-asbesthaltigem Fasermaterial enthält, das aus der Gruppe ausgewählt ist, die aus Celluloseholzfasern, nicht-hölzernen Cellulosefasern, Mineralwolle, Stahlfasern, synthetischen Polymerfasern wie Polyamiden, Polyester, Polypropylen, Polymethylpenten, Polyacrylnitril, Polyacrylamid, Viskose, Nylon, PVC, PVA, Rayon und Glas, Keramik oder Kohlenstoff und Mischungen davon besteht.

55 58. Formulierung nach Anspruch 57, wobei die Fasern Cellulosefasern sind, die gebleicht, ungebleicht, teilweise gebleicht oder Mischungen davon sind.

59. Formulierung nach einem der Ansprüche 56 bis 58, wobei die Menge an faserartigem Material zwischen 2 und 15

Gew.-% trockener Zutaten liegt.

60. Formulierung nach einem der Ansprüche 56 bis 59, wobei die Menge an faserartigem Material zwischen 5 und 14 Gew.-% trockener Zutaten liegt.

5 61. Formulierung nach einem der Ansprüche 34 bis 60, die ferner 0 bis 40 Gew.-% trockener Zutaten an anderen Zusätzen enthält, die ausgewählt sind aus der Gruppe, die aus Füllstoffen, Brandverzögerern, Eindickern, Farbstoffen, Pigmenten, wasserdichtenden Mitteln, wasserreduzierenden Mitteln, wasserhaltenden Mitteln, Abbinderratenmodifizierem, Härtem, Füllstoffhilfsmitteln, Plastifizierungsmitteln, Dispergiermitteln, Treibmitteln, Entschäumem, Flockungsmitteln, Wasserabdichtungsmitteln, Dichtemodifizierern und Mischungen davon besteht.

10 62. Formulierung nach einem der Ansprüche 34 bis 61, die ferner 0 bis 40 Gew.-% trockener Zutaten an anderen Zusätzen enthält, die ausgewählt sind aus der Gruppe, die aus Mineraloxiden, Mineralhydroxiden und Tonen, Metalloxiden und Hydroxiden, Magnesit, Dolomit, Aluminiumpulver, Aluminiumoxidtrihydrat, Kaolin, Glimmer, Metakaolin, Quarzstaub, Calciumcarbonat, Wollastonit, Methylcellulose und Mischungen davon besteht.

15 63. Zementöses Produkt, das das im Autoklaven gehärtete Reaktionsprodukt der Formulierung nach einem der Ansprüche 34 bis 62 aufweist.

20 **Revendications**

1. Procédé de formation d'un produit cimentaire comprenant l'ajout d'un matériau cimentaire, d'un matériau siliceux et d'un matériau à faible densité apparente, à de l'eau, de façon à former une bouillie formant un article vert profilé à partir de la bouillie, et la cuisson de l'article dans un autoclave, *caractérisé en ce que le matériau à faible densité apparente est un mélange de silicate de calcium hydraté et d'un réactif siliceux n'ayant pas réagi.*

25 2. Procédé selon la revendication 1, dans lequel le matériau à faible densité apparente a une densité apparente comprise entre 0,06 et 0,3 g/cm<sup>3</sup>.

30 3. Procédé selon la revendication 1 ou la revendication 2, dans lequel le matériau à faible densité est fourni en :

35 faisant réagir un réactif siliceux avec un réactif calcaire en présence d'eau sous pression et à une température élevée, dans lesquels au moins 90 % en poids du réactif siliceux a une taille de particules inférieure à 100 microns (100 µm).

40 4. Procédé selon l'une quelconque des revendications précédentes, dans lequel des additifs fibreux et/ou autres sont ajoutés à la bouillie avant la formation de l'article vert profilé.

45 5. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'article vert profilé est formé par le procédé Hatschek.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'article vert profilé est formé par un procédé de filtration.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'article vert profilé est formé par un moulage par injection.

50 8. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'article vert profilé est formé par un procédé par extrusion.

9. Procédé selon l'une quelconque des revendications 3 à 8, dans lequel on arrête la réaction avant la fin de la conversion des réactifs en silicate de calcium hydraté.

55 10. Procédé selon l'une quelconque des revendications 3 à 9, dans lequel la réaction est conduite pendant moins de 4 heures.

11. Procédé selon l'une quelconque des revendications 3 à 10, dans lequel la réaction est conduite pendant une durée allant jusqu'à 2 heures, et dans lequel au moins 80 % du matériau réactif calcaire est converti en hydroxyde de silicate de calcium.

5 12. Procédé selon l'une quelconque des revendications 3 à 11, dans lequel, avant ou pendant la réaction, on ajoute de l'eau, en une quantité allant jusqu'à 30 fois le poids total des réactifs siliceux et calcaire.

10 13. Procédé selon l'une quelconque des revendications 3 à 12, dans lequel la réaction est conduite à une température comprise entre 120 et 250 °C.

15 14. Procédé selon l'une quelconque des revendications 3 à 13, dans lequel la réaction est conduite à une température comprise entre 160 et 180 °C.

16. Procédé selon l'une quelconque des revendications 3 à 14, dans lequel la réaction est conduite sous une pression comprise entre 200 et 4000 kPa.

20 17. Procédé selon l'une quelconque des revendications 3 à 16, dans lequel on fait réagir le réactif calcaire et le réactif siliceux avec un rapport molaire CaO/SiO<sub>2</sub> compris entre 0,1 et 1,2.

25 18. Procédé selon l'une quelconque des revendications 3 à 17, dans lequel on fait réagir le réactif calcaire et le réactif siliceux avec un rapport molaire CaO/SiO<sub>2</sub> compris entre 0,3 et 0,8.

19. Procédé selon l'une quelconque des revendications 3 à 18, dans lequel le réactif siliceux a une taille de particules à 90 % en poids inférieure à 70 microns (70 µm).

30 20. Procédé selon l'une quelconque des revendications 3 à 19, dans lequel le réactif siliceux a une taille de particules à 90 % en poids inférieure à 50 microns (50 µm).

21. Procédé selon l'une quelconque des revendications précédentes, dans lequel le réactif siliceux et/ou le matériau siliceux est (sont) amorphe(s).

35 22. Procédé selon l'une quelconque des revendications précédentes, dans lequel le réactif siliceux et/ou le matériau siliceux est (sont) cristallin(s).

23. Procédé selon l'une quelconque des revendications 3 à 22, dans lequel le réactif calcaire est de la chaux.

40 24. Procédé selon l'une quelconque des revendications 3 à 23, dans lequel le réactif calcaire est de la chaux vive.

25. Procédé selon l'une quelconque des revendications 3 à 24, dans lequel le réactif calcaire contient plus de 90 % de CaO.

45 26. Procédé selon l'une quelconque des revendications précédentes, dans lequel le réactif siliceux et/ou le matériau siliceux est (sont) sélectionné(s) dans le groupe consistant en une silice, en quartz, une quartzite, un sable de quartzite, une terre de diatomées, une fumée de silice, des cendres de balle de riz, une cendre volante, un laitier de haut fourneau, un laitier granulé, un laitier d'acier, un laitier cristallin ou lentement refroidi à l'air, une silice géothermique et les mélanges de ces produits.

50 27. Procédé selon l'une quelconque des revendications 3 à 26, dans lequel le réactif siliceux et le réactif calcaire ont pour origine un seul matériau source.

28. Procédé selon l'une quelconque des revendications 3 à 26, dans lequel le réactif siliceux et le réactif calcaire ont pour origine des matériaux sources séparés.

55 29. Procédé selon l'une quelconque des revendications précédentes, dans lequel le matériau cimentaire est sélectionné dans le groupe consistant en un ciment, une chaux, un matériau contenant de la chaux, un ciment Portland,

un ciment blanchâtre, un ciment mélangé, une chaux hydratée ou des mélanges de ces produits.

30. Procédé selon l'une quelconque des revendications précédentes, dans lequel le matériau cimentaire et le matériau siliceux ont pour origine un seul matériau source.

5 31. Procédé selon l'une quelconque des revendications précédentes, dans lequel le matériau cimentaire et le matériau siliceux ont pour origine des matériaux sources séparés.

10 32. Procédé selon l'une quelconque des revendications précédentes, dans lequel le produit cimentaire est traité par un silane, un siloxane et/ou une silicone, afin de réduire ses caractéristiques d'absorption de l'eau et de perméabilité à l'eau de surface.

15 33. Procédé selon l'une quelconque des revendications précédentes, dans lequel le matériau à faible densité apparente est ajouté en quantités suffisantes, de telle sorte que le produit cimentaire obtenu a une densité comprise entre 0,5 et 1,2 g/cm<sup>3</sup>.

34. Formulation permettant de préparer un produit cimentaire comprenant :

20 un matériau cimentaire

un matériau siliceux, et

un matériau à faible densité apparente, caractérisé en ce que le matériau à faible densité apparente est un mélange de silicate de calcium hydraté et d'un réactif siliceux n'ayant pas réagi.

25 35. Formulation selon la revendication 34, dans laquelle le matériau à faible densité apparente a une densité apparente comprise entre 0,06 et 0,3 g/m<sup>3</sup>.

30 36. Formulation selon la revendication 34, dans laquelle le matériau à faible densité apparente est produit en faisant réagir un réactif siliceux avec un réactif calcaire en présence d'eau sous pression et à une température élevée afin de former le matériau à faible densité apparente, au moins 90 % en poids du réactif siliceux ayant une taille de particule inférieure à 100 microns (100 µm).

37. Formulation selon l'une quelconque des revendications 34 à 36, comprenant en outre de l'eau.

35 38. Formulation selon l'une quelconque des revendications 34 à 37, dans laquelle le matériau à faible densité est ajouté en une quantité allant jusqu'à 80 % en poids des ingrédients secs.

39. Formulation selon l'une quelconque des revendications 34 à 38, dans laquelle le matériau à faible densité est ajouté en une quantité pouvant atteindre 50 % en poids des ingrédients secs.

40 40. Formulation selon l'une quelconque des revendications 34 à 39, dans laquelle le matériau à faible densité est ajouté dans des quantités suffisantes, de sorte que le produit cimentaire a une densité comprise entre 0,5 et 1,2 g/cm<sup>3</sup>.

45 41. Formulation selon l'une quelconque des revendications 34 à 40, dans laquelle la quantité de matériau siliceux est comprise entre 10 et 80 % en poids des ingrédients secs.

42. Formulation selon l'une quelconque des revendications 34 à 41, dans laquelle la quantité de matériau siliceux est comprise entre 40 et 65 % en poids des ingrédients secs.

50 43. Formulation selon l'une quelconque des revendications 34 à 42, dans laquelle le réactif siliceux et/ou le matériau siliceux est (sont) sélectionné(s) dans le groupe consistant en une silice, un quartz, une quartzite, un sable de quartzite, une terre de diatomées, une fumée de silice, des cendres de balle de riz, une cendre volante, un laitier de haut fourneau, un laitier granulé, un laitier d'acier, un laitier cristallin ou lentement refroidi à l'air, une silice géothermique et les mélanges de ces produits.

55 44. Formulation selon l'une quelconque des revendications 34 à 43, dans laquelle le réactif siliceux et/ou le matériau siliceux est (sont) amorphes.

45. Formulation selon l'une quelconque des revendications 34 à 43, dans laquelle le réactif siliceux et/ou le matériau siliceux est (sont) cristallins.

5 46. Formulation selon l'une quelconque des revendications 34 à 45, dans laquelle la quantité de matériau cimentaire est comprise entre 10 et 80 % en poids des ingrédients secs.

47. Formulation selon l'une quelconque des revendications 34 à 46, dans laquelle la quantité de matériau cimentaire est comprise entre 30 et 40 % en poids des ingrédients secs.

10 48. Formulation selon l'une quelconque des revendications 34 à 47, dans laquelle le matériau cimentaire est sélectionné dans le groupe consistant en un ciment, une chaux, un matériau contenant de la chaux, un ciment Portland, un ciment blanchâtre, un ciment mélangé, une chaux hydratée ou des mélanges de ces produits.

15 49. Formulation selon l'une quelconque des revendications 34 à 48, dans laquelle le matériau siliceux et le matériau cimentaire ont pour origine un seul matériau source.

50. Formulation selon l'une quelconque des revendications 34 à 48, dans laquelle le matériau siliceux et le matériau cimentaire ont pour origine des matériaux sources séparés.

20 51. Formulation selon l'une quelconque des revendications 36 à 50, dans laquelle le réactif calcaire est de la chaux.

52. Formulation selon l'une quelconque des revendications 36 à 51, dans laquelle le réactif calcaire est de la chaux vive.

25 53. Formulation selon l'une quelconque des revendications 36 à 52, dans laquelle le réactif calcaire contient plus de 90 % de CaO.

54. Formulation selon l'une quelconque des revendications 36 à 53, dans laquelle le réactif siliceux et le réactif calcaire ont pour origine un seul matériau source.

30 55. Formulation selon l'une quelconque des revendications 36 à 53, dans laquelle le réactif siliceux et le réactif calcaire ont pour origine des matériaux sources séparés.

56. Formulation selon l'une quelconque des revendications 34 à 55, comportant en outre entre 0 et 25 % en poids des ingrédients secs, d'un matériau de fibres d'amiante.

35 57. Formulation selon l'une quelconque des revendications 34 à 55, comportant en outre entre 0 et 25 % en poids des ingrédients secs, d'un matériau fibreux ne comportant pas d'amiante, sélectionné dans le groupe consistant en fibres ligneuses de cellulose, en fibres non ligneuses de cellulose, en laine minérale, en fibres d'acier, en fibres polymères synthétiques, comme les polyamides, les polyesters, le polypropylène, le polyméthylpentène, le polyacrylonitrile, le polyacrylamide, la viscose, le nylon, le PVC, le PVA, la rayonne et le verre, la céramique ou le carbone et des mélanges de ceux-ci.

40 58. Formulation selon la revendication 57, dans laquelle les fibres sont des fibres de cellulose qui sont blanchies, non blanchies, partiellement blanchies ou des mélanges de ces produits.

59. Formulation selon l'une quelconque des revendications 56 à 58, dans laquelle la quantité de matériau fibreux est comprise entre 2 et 15 % en poids des ingrédients secs.

50 60. Formulation selon l'une quelconque des revendications 56 à 59, dans laquelle la quantité de matériau fibreux est comprise entre 5 et 14 % en poids des ingrédients secs.

61. Formulation selon l'une quelconque des revendications 34 à 60, comportant en outre entre 0 et 40 % en poids des ingrédients secs, d'autres additifs sélectionnés dans le groupe consistant en les charges de remplissage, les produits ignifuges, les agents épaississants, les colorants, les pigments, les agents d'étanchéité à l'eau, les agents réducteurs d'eau, les agents de rétention d'eau, les agents modificateurs du fargeage, les agents durcisseurs, les agents d'aide dans les charges de remplissage, les plastifiants, les dispersants, les agents moussants, les agents anti-mousse, les agents flocculants, les agents hydrofuges, les agents modificateurs de la densité et des mélanges

de ces additifs.

5       **62.** Formulation selon l'une quelconque des revendications 36 à 61, comprenant en outre entre 0 et 40 % en poids  
des ingrédients secs, ou d'autres additifs sélectionnés dans le groupe consistant en les oxydes minéraux, les  
hydroxydes minéraux, et les argiles, les oxydes métalliques et les hydroxydes métalliques, la magnésite, la dolomite,  
la poudre d'aluminium, le trihydrate d'alumine, le kaolin, le mica, le métakaolin, la fumée de silice, le carbonate  
de calcium, la wollastonite, la méthylcellulose et les mélanges de ces additifs.

10      **63.** Produit cimentaire comprenant le produit de réaction de cuisson à l'autoclave de la formulation selon l'une quel-  
conque des revendications 34 à 62.

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